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- (71) Applicant (*for all designated States except US*): EVEREADY BATTERY COMPANY, INC. [US/US]; P.O. Box 450777, 25225 Detroit Road, Westlake, OH 44145 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): JIN, Zhihong [US/US]; 1106 Starlight Lane, Cottage Grove, WI 53527 (US). KENNEDY, John, H. [US/US]; 5357 Agana Drive, Santa Barbara, CA 93111-1601 (US).
- (74) Agent: TOYE, Russell, H., Jr.; Eveready Battery Company, Inc., P.O. Box 450777, 25225 Detroit Road, Westlake, OH 44145 (US).
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(54) Title: PERFORMANCE ENHANCING ADDITIVES FOR ELECTROCHEMICAL CELLS

(57) Abstract: Alkaline battery cells comprising an anode, a cathode, a separator between the anode and the cathode, and an electrolyte are provided with an n-type metal oxide additive that improves electrochemical performance. The n-type metal oxide additive is either a doped metal oxide comprising a metal oxide modified by incorporation of a dopant, or a reduced metal oxide. The metal oxide may be selected from the group consisting of BaTiO<sub>3</sub>, K<sub>2</sub>TiO<sub>3</sub>, CoTiO<sub>3</sub>, SrTiO<sub>3</sub>, CaTiO<sub>3</sub>, MgTiO<sub>3</sub>, SiO<sub>2</sub>, CaO, TiO<sub>2</sub>, CoO, Co<sub>3</sub>O<sub>4</sub>, ZnO, SnO, SnO<sub>2</sub>, PbO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>·3ZrO<sub>3</sub>, Bi<sub>12</sub>TiO<sub>20</sub>, Fe<sub>2</sub>O<sub>3</sub>·TiO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, CaWO<sub>4</sub>, ZnMn<sub>2</sub>O<sub>4</sub>, and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. Examples of dopant disclosed are: NbO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub>, GeO<sub>2</sub>, ZrO<sub>2</sub>, SnO<sub>2</sub>, ThO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, LiNiO<sub>2</sub>, and P<sub>2</sub>O<sub>5</sub>, In<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>5</sub>.

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PERFORMANCE ENHANCING ADDITIVES FOR ELECTROCHEMICAL CELLSFIELD OF THE INVENTION

This invention relates to electrochemical cells, particularly to additives for the anodes, cathodes and/or electrolytes of such cells for the purpose of enhancing electrochemical performance of the cells.

BACKGROUND OF THE INVENTION

Battery manufacturers are continually trying to improve the electrochemical performance of their batteries, since even relatively small improvements of performance characteristics such as discharge capacity, cycle life and shelf life can provide advantages in a highly competitive market. At the same time, the current requirements of electronic devices that are powered by batteries are increasing, and the capacity at higher discharge rates is becoming a more important characteristic for these batteries. This is particularly true of both primary and rechargeable alkaline batteries.

One approach that has been used to improve the discharge capacity and/or cycle life of electrochemical cells is to use performance enhancing additives in the negative electrode, positive electrode and/or electrolyte. Such additives may affect these improvements by reducing the internal resistance of the cells, increasing ionic conductivity, preventing the formation of undesirable byproducts, and so forth.

Evans (US Patent No. 4,465,747) discloses a nonaqueous cell with an organic solvent electrolyte and a cathode containing  $\text{MnO}_2$  and a minor amount of an additive selected from the group consisting of borates, silicates, molybdates, phosphates, aluminates, niobates, tantalates, titanates, vanadates, zirconates, manganates, cobaltates and tungstenates of alkali metals or alkaline earth metals. Langan (US Patent No. 4,478,921) discloses a nonaqueous cell with a cathode containing  $\text{MnO}_2$  and a minor amount of  $\text{MnCO}_3$ . The purpose of these additives is to minimize the increase in internal impedance of the cell during storage or discharge. The additive is believed to prevent degradation of the electrolyte caused by reaction of the electrolyte with

surface acidic groups on the  $\text{MnO}_2$  or incompletely neutralized salts used in preparing the electrolyte solution.

5 Taucher et al. (PCT Patent Publication No. WO 93/12551) disclose primary and rechargeable alkaline  $\text{Zn/MnO}_2$  cells with barium compounds (e.g., oxide, hydroxide or sulfate) added to the cathode to improve cell capacity. The barium compound slows down the formation of hetaerolite, which cannot participate in the cycling process and tends to expand and destroy the cathode structure. Cathode additives for improving the capacity of alkaline  $\text{Zn/MnO}_2$  cells have been disclosed. Swierbut et al. disclose the use of one or more of  $\text{SnO}_2$ ,  $\text{Fe}_2\text{O}_3\text{-TiO}_2$ ,  $\text{TiO}_2$  (P-25),  $\text{BaTiO}_3$ ,  $\text{K}_2\text{TiO}_3$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{SnO}$  in US Patent No. 5,599,644. Nardi et al. disclose the use of at least one of  $\text{SrTiO}_3$  or  $\text{CoTiO}_3$  in US Patent No. 5,895,734.  $\text{CaWO}_4$ ,  $\text{MgTiO}_3$ ,  $\text{BaTiO}_3$ ,  $\text{CaTiO}_3$ ,  $\text{ZnMn}_2\text{O}_4$  and  $\text{Bi}_{12}\text{TiO}_{20}$  are disclosed by Davis et al. in US Patent No. 5,532,085. Mieczkowska et al. disclose the use of  $\text{Bi}_2\text{O}_3$ ,  $\text{PbO}_2$ ,  $\text{SnO}_2$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{CoO}$ ,  $\text{Bi}_2\text{O}_3\cdot 3\text{ZrO}_3$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  in US Patent No. 5,516,604. In US Patent No. 5,342,712, Mieczkowska et al. teach that the useful service life of primary alkaline  $\text{Zn/MnO}_2$  cells can be extended as a result of increased mobility of ionic flow during discharge by adding anatase  $\text{TiO}_2$  to the cathode.

15 While there may be advantages to using such additives, in many cases the advantages can be at least partially offset, particularly on heavy drains, by the relatively high resistivities of the additives which increase the internal resistance of the cell.

It is known that the physical and electrochemical properties of semiconductor materials such as  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{SnO}_2$  can be modified by doping those materials with other cations. This approach has been used to modify materials for use in the fields of semiconductors, photoelectrochemistry and solid state sensors. For example, Unexamined Japanese Patent Publication No. 10-316,429 discloses that anatase  $\text{TiO}_2$  is suitable for use as a white electroconductive powder in the manufacture of semiconductors if it is doped with zinc or aluminum and its surface is coated with an electroconductive film of metal oxide. Karakitsou et al. disclose the use of cation doped  $\text{TiO}_2$  exhibiting improved performance as a photocatalyst in water cleavage in the *Journal of Physical Chemistry*, 1993, vol. 97, pages 1184-1189. Katayama et al. disclose the use of  $\text{Nb}_2\text{O}_5$ -doped  $\text{TiO}_2$  ceramics exhibiting improved humidity sensitivity.

### SUMMARY OF THE INVENTION

This invention provides electrochemical cells exhibiting improved discharge capacity, especially on high current drains; and rechargeable electrochemical cells exhibiting improved cycle life.

5        One aspect of the invention is an electrochemical battery cell comprising an anode, a cathode, a separator between the anode and cathode, and an electrolyte, wherein at least one of the anode, cathode and electrolyte contains an n-type metal oxide additive.

### BRIEF DESCRIPTION OF THE DRAWINGS

10       Fig. 1 is a graph of dry cathode resistance as a function of cathode compression for cathodes made according to the present invention.

Fig. 2 is a comparison of relative discharge durations of miniature cells with cathodes made according to the present invention.

Fig. 3 is a comparison of relative discharge durations of flooded half cells with cathodes made according to the present invention.

15       Fig. 4 is a comparison of discharge curves of flooded half cells having cathodes made according to the prior art and flooded half cells having cathodes made according to the present invention.

20       Fig. 5 is a comparison of discharge curves of flooded half cells having cathodes made according to the prior art and flooded half cells having cathodes made according to the present invention.

Fig. 6 is a X-ray diffraction pattern comparing anatase titanium dioxide, rutile titanium dioxide and a conductive, niobium-doped titanium oxide in accordance with the invention.

25       Fig. 7 is a comparison of the X-ray diffraction pattern of a commercially available Magneli material with the diffraction pattern of a conductive, niobium-doped titanium oxide in accordance with the invention.

Fig. 8 is a cutaway view of an alkaline battery employing an additive in accordance with the invention.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

30       It has been found that, by modifying performance-enhancing additives to electrochemical cells to make the additives n-type materials, the performance of electrochemical cells can be

further enhanced. In particular, additives which improve discharge capacity, especially on high rate discharge, have been found to be even more effective in doing so when reduced with hydrogen or doped with cations to reduce their resistivities.

5 An n-type semiconductor is a semiconductor (a non-metallic material that has a filled valence band at 0 K and a relatively narrow energy band gap with room temperature electrical conductivity ranging between about  $10^{-6}$  and  $10^4$  (ohm-m) $^{-1}$ ) for which the predominant charge carriers responsible for electrical conduction are electrons.

10 Normally, donor impurity atoms give rise to the excess electrons, which contribute to the conductivity. Another way to produce excess electrons is by heat treating under a reducing atmosphere, resulting in a non-stoichiometric composition with excess metal content (e.g.,  $\text{Ti}_{1+x}\text{O}_2$ ).

Electrochemical cells of this invention include both primary and rechargeable cells for use in batteries. The cells may have aqueous or nonaqueous electrolytes. Examples of cell types with nonaqueous electrolytes are  $\text{Li/MnO}_2$  and lithium ion cells. Examples of cells having an aqueous electrolyte include cells having an alkaline electrolyte, such as an aqueous solution of KOH and/or NaOH. Other cells having an aqueous electrolyte include zinc chloride carbon-zinc cells with electrolytes comprising aqueous solutions of  $\text{NH}_4\text{OH}$  and  $\text{ZnCl}_2$ . Examples of suitable electrochemical systems having an aqueous alkaline electrolyte include  $\text{Zn/MnO}_2$ ,  $\text{Mg/MnO}_2$ ,  $\text{Al/MnO}_2$ ,  $\text{Zn/Ag}_2\text{O}$ ,  $\text{Zn/HgO}$ ,  $\text{Ni/Cd}$ ,  $\text{NiMeH}$ , and  $\text{NiH}$ .  $\text{Zn/MnO}_2$  is a preferred system.

25 Examples of additives that are suitable for use in the invention include metal oxides which are stable in the internal environment of the cell and can be modified to n-type materials, such as by reduction (e.g., with hydrogen) or by doping with cations of other elements. Preferred additives are those which, without being modified, have performance-enhancing effects on electrochemical cells. Preferred additives generally, though not always, have a  $2^+$  to  $6^+$  valence cation. Examples of preferred additives include  $\text{BaTiC}_3$ ,  $\text{K}_2\text{TiO}_3$ ,  $\text{CoTiO}_3$ ,  $\text{SrTiO}_3$ ,  $\text{CaTiO}_3$ ,  $\text{MgTiO}_3$ ,  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{TiO}_2$ ,  $\text{CoO}$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{ZnO}$ ,  $\text{SnO}$ ,  $\text{SnO}_2$ ,  $\text{PbO}_2$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3 \cdot 3\text{ZrO}_3$ ,  $\text{Bi}_{12}\text{TiO}_{20}$ ,  $\text{Fe}_2\text{O}_3\text{-TiO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{CaWO}_4$ ,  $\text{ZnMn}_2\text{O}_4$ ,  $\text{ReO}_3$ ,  $\text{TiO}$ ,  $\text{ErO}_2$ ,  $\text{VO}_2$ ,  $\text{Ti}_2\text{O}_3$ ,  $\text{VO}$ .

$\text{Fe}_3\text{O}_4$ ,  $\text{FeO}$ ,  $\text{V}_2\text{O}_3$ ,  $\text{ReO}_2$ ,  $\text{NbO}$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ . The additives  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{SnO}_2$  are preferred, with  $\text{TiO}_2$  being the most preferred. When  $\text{TiO}_2$  is used as an additive in the present invention, the  $\text{TiO}_2$  may be either anatase or rutile.

Suitable dopants are incorporated into the metal oxide structure to produce a doped additive (modified additive) that is an n-type material which is stable in the internal environment of the cell. Cations of the dopant may be incorporated into the metal oxide structure by substitution for a portion of the cations of the metal oxide, by occlusion into the spaces of the lattice structure of the metal oxide, or by replacement of dopant cations for some of the cations in the lattice structure. A preferred dopant will modify the physical and/or electrochemical properties of the additive in a desired way, preferably by reducing the resistivity of the additive, improving the ionic exchange characteristics of the additive, and/or reducing the formation of undesired corrosion or discharge reaction byproducts (such as hydrogen gas). Examples of dopants that are suitable for doping  $\text{TiO}_2$  used as an additive in an alkaline cell include  $\text{NbO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{WO}_3$ ,  $\text{GeO}_2$ ,  $\text{ZrO}_2$ ,  $\text{SnO}_2$ ,  $\text{ThO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{LiNiO}_2$  and  $\text{P}_2\text{O}_5$ , with  $\text{Nb}_2\text{O}_5$  being a preferred dopant. Suitable dopants for  $\text{SnO}_2$  include  $\text{In}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{WO}_3$  and  $\text{P}_2\text{O}_5$ .

The optimum amount of dopant depends on the additive and the electrochemical system of the cell. Phase Diagrams for Ceramists, Second Edition 1969, The American Ceramic Society, Columbus, Ohio, 1964, contains phase diagrams for many metal oxides and potential dopants. This can be useful in selecting dopants and suitable metal oxide dopant ratios. Generally, at least about 0.01 to less than about 50 mol percent dopant cation, based on the total cation content of the doped metal oxide, is suitable for use in the present invention. Preferably about 0.1 to about 30 mol percent, and more preferably about 0.1 to about 20 mol percent dopant cation is used. For an alkaline  $\text{Zn/MnO}_2$  cell with  $\text{TiO}_2$  additive, the preferred amount of dopant is about 1 to about 20 mol percent, more preferably about 5 to about 15 mol percent and most preferably about 10 mol percent based on the total cation content of the doped  $\text{TiO}_2$ . For example, when  $\text{TiO}_2$  is doped with  $\text{Nb}_2\text{O}_5$ , a preferred amount of  $\text{Nb}_2\text{O}_5$  dopant is about 5 mol percent of the doped  $\text{TiO}_2$ , which is equivalent to 10 mol percent Nb doped into  $\text{TiO}_2$ ,

based on the total Nb + Ti content. A preferred niobium-doped  $\text{TiO}_2$  for use in an alkaline Zn/MnO<sub>2</sub> cell is, therefore,  $\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_2$ . When SnO<sub>2</sub> is the additive, the mol percent of the dopant required may be significantly less than with  $\text{TiO}_2$ .

The doped or modified additive may initially be put into one or more of the negative electrode, positive electrode, and electrolyte. After the cell is assembled, the modified additive may migrate to other parts of the cell. The preferred initial location of the modified additive can depend upon a number of factors, including the cell component to be affected, the desired type of effect, and the mobility of the modified additive. Preferred additives are insoluble in the electrolyte.

The amount of modified additive used in the cell depends on a number of factors. The preferred amount of unmodified additive is a good indicator of the preferred amount of modified additive. However, by increasing the effectiveness of the additive, it may be possible to achieve the same effect with less modified additive, or, if the modified additive has a lower resistivity, it may be possible to add more of the modified additive without increasing the internal resistance of the cell to an undesirable level. Preferably the amount of modified additive is no more than about 20 wt%, based on the weight of active material in either the anode or the cathode, whichever contains less. If the modified additive has sufficient electrical conductivity, it may be possible to reduce the amount of inert conductive material used in the electrode and still further increase the capacity of the cell.

Any suitable method may be used for doping the metal oxide of the present invention.  $\text{TiO}_2$  is a preferred cathode additive. Examples of suitable methods of doping  $\text{TiO}_2$  are disclosed in US Patent No. 5,419,824; US Patent No. 5,364,508; *Journal of Physical Chemistry*, 97 (1993) 1184-1189; *Sensors and Actuators A*, 24 (1990) 55-60; *Sensors and Actuators B*, 18-19 (1994) 474-477; and *Solar Energy Materials*, 2 (1980) 413-421.

An alternative to doping the metal oxide additive is to modify the metal oxide by reducing it, e.g., with hydrogen, to produce an n-type material. When the metal oxide is  $\text{TiO}_2$ , either anatase or rutile  $\text{TiO}_2$  may be used as a starting material. Suitable n-type  $\text{TiO}_2$  may also be either anatase or rutile, depending upon the method used to reduce the  $\text{TiO}_2$ .

A preferred embodiment of the present invention is an alkaline  $\text{Zn/MnO}_2$  cell with  $\text{TiO}_2$  added to the cathode. In the examples below,  $\text{TiO}_2$  is doped with  $\text{Nb}_2\text{O}_5$  or reduced with  $\text{H}_2$  to lower its resistivity.

The novel compounds of this invention are reduced doped titanium oxides that are highly  
5 conductive (have a low electrical resistivity) as compared with conventional titanium dioxide additives used for enhancing performance of electrochemical battery cells. A conductive form of titanium oxide for alkaline battery cathodes is desired to improve the conductivity of the cathode while continuing to provide the performance improvement associated with traditional insulating titanium dioxide additives. The novel reduced doped titanium oxides in accordance with this  
10 aspect of the invention are represented by the formula  $\text{Ti}_{1-x}\text{M}_x\text{O}_{2-y}$ , where M is an element having an octagonal coordination structure, x is from about 0.01 to about 0.5, and y is from about 0.05 to about 0.25. The conductive, doped titanium oxides in accordance with this aspect of the invention have an electrical conductivity that is comparable to that of the Magneli phase substoichiometric titanium oxides. However, the conductive, doped titanium oxides in  
15 accordance with this aspect of the invention have an expanded rutile crystal structure, that is substantially the same as the rutile structure of conventional insulating titanium dioxide additives that provide significant performance improvements in alkaline electrochemical battery cells, whereas the Magneli phase substoichiometric titanium oxides have a significantly different crystal structure.

20 Element M in the conductive, doped titanium oxides of this invention is selected from elements that can be substituted for a titanium atom in the rutile crystal lattice. Such elements are generally metals having an octagonal coordination structure. Suitable elements M include but are not limited to niobium, vanadium, tantalum, tungsten, zirconium, hafnium, iron, cobalt, nickel, chromium and molybdenum, with niobium being preferred.

25 The value of x is from about 0.01 to about 0.5, with values from about 0.05 to about 0.2 being preferred, and a value of from about 0.07 to about 0.2 being more preferred. Conductive, doped titanium oxide compounds in accordance with the invention are believed to exhibit the best performance enhancing characteristics when used as an additive for a manganese dioxide electrode when the value of x is about 0.1.



The value of  $y$  for the conductive, doped titanium oxides represented by the above formula is from about 0.05 to about 0.25, preferably from about 0.1 to about 0.25, and more preferably from about 0.15 to about 0.25. In general, higher values of  $y$  are more electrically conductive (have a lower electrical resistivity). Accordingly, compounds having a value of  $y$  that approaches 0.25 are preferred.

Titanium dioxide occurs in nature in three crystalline forms: anatase, brookite, and rutile. Rutile is the thermodynamically stable form at all temperatures. Calorimetric studies have demonstrated that rutile is more stable than anatase and that brookite has a stability intermediate between anatase and rutile.

Fig. 6 compares the X-ray diffraction patterns of anatase titanium dioxide, rutile titanium dioxide, and a conductive, niobium-doped titanium oxide (NTO) in accordance with an aspect of this invention. The diffraction peaks for NTO are shifted to a slightly lower  $2\theta$  value compared with pure rutile titanium dioxide. From Bragg's Law ( $n\lambda = 2d \sin \theta$ ), the lower  $2\theta$  value corresponds to a higher  $d$  spacing and an expanded lattice. The doping of  $\text{Nb}^{5+}$  for  $\text{Ti}^{4+}$  in the rutile structure causes this expanded lattice for NTO. The lattice parameters for NTO may be measured from the powder diffraction pattern and are compared with pure rutile titanium dioxide in Table 1. The space groups and lattice parameters for anatase titanium dioxide are also shown to further highlight the differences among the materials.

Table 1

Material	Space Group	$a(\text{\AA})$	$c(\text{\AA})$
NTO	$P4_2/mnm$	4.619	2.971
Rutile- $\text{TiO}_2$	$P4_2/mnm$	4.593	2.959
Anatase- $\text{TiO}_2$	$I4_1/amd$	3.785	9.514

The crystal structures of the Magneli phases are comprised of rutile titanium dioxide blocks separated by  $\text{TiO}$  layers. The number of  $\text{TiO}$  layers increases as  $n$  (in the formula  $\text{Ti}_n\text{O}_{2n-1}$ ) decreases from 10 to 4. The diffraction pattern of a commercially available Magneli phase material is compared with the diffraction pattern of NTO in Fig. 7. The two materials

clearly have different structures. NTO retains the rutile titanium dioxide structure upon loss of oxygen, whereas the Magneli phase material transforms to a different structure as it loses oxygen.

Anatase titanium dioxide and rutile titanium dioxide are white powders, whereas NTO and commercially available Magneli materials are dark blue-black. The color of a material may

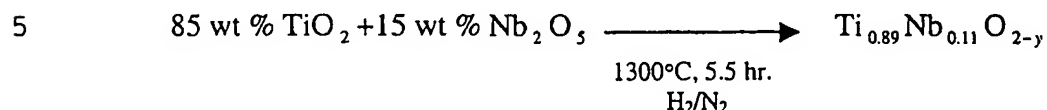
5 be further described more quantitatively using the Munsell notation. The Munsell notation system is described in *The Munsell Book of Color*, Munsell Color, Macbeth Division of Kollmorgen Instruments Corporation, New York. The Munsell Color-order system is a way of precisely specifying colors and showing the relationship among colors. Every color has three qualities or attributes: hue, value and chroma. Munsell established numerical scales with  
10 visually uniform steps for each of these attributes. *The Munsell Book of Color* displays a collection of colored chips arranged according to the scales. Each chip is identified numerically using these scales. The color of any material can be identified by comparing it to the chips under proper illumination and viewing conditions. The colors are then identified by hue, value and chroma. These attributes are given the symbols H, V and C, and are written in a form "H V/C,"  
15 which is called the Munsell notation. Using the Munsell notation system, NTO may be described as having a hue of 10B, a value of 3, and a chroma of 2. The notation for a neutral color, under the Munsell notation system, is written as "N V/." The chroma of a neutral color is 0, but is customarily omitted from the notation. The Munsell color notation for anatase titanium dioxide is "N 9/."

20 The conductive, doped titanium oxides in accordance with an aspect of this invention exhibit significantly improved electrical conductivity as compared with anatase titanium dioxide.

The improved conductivity is attributed to the loss of oxygen from the lattice upon heating in a reducing atmosphere. The resistivity of NTO is comparable to that of commercially available Magneli phase materials. Anatase titanium dioxide has a resistivity of about  $10^6$  ohm-cm. The  
25 commercially available Magneli phase materials and the conductive doped titanium oxide materials in accordance with an aspect of this invention have electrical resistivities that are several orders of magnitude less than anatase titanium dioxide. In particular, the resistivities of the conductive, doped titanium oxide materials in accordance with an aspect of this invention are less than 100 ohm-cm, and are preferably about 10 ohm-cm or less.

The conductive, doped titanium oxides in accordance with an aspect of this invention are prepared by high temperature reaction of titanium dioxide and an oxide of M in a reducing atmosphere to form an electrically conductive ceramic powder with the formula  $Ti_{1-x}M_xO_{2-y}$ .

As an example, the reaction of titanium dioxide with  $Nb_2O_5$  is represented as follows:



wherein y is defined above.

The novel conductive doped titanium oxide materials of this invention may be prepared by intimately mixing a titanium dioxide with an oxide of an element selected from niobium, vanadium, tantalum, tungsten, zirconium, hafnium, iron, cobalt, nickel, chromium and molybdenum. A suitable degree of mixing may be achieved by wet mechanical mixing or by dry mechanical mixing. It is highly desirable to achieve intimate mixing to minimize the distance that material must travel in the solid state. Stated differently, the more intimate the mixing of the titanium dioxide and the dopant, the faster the reaction will progress to completion. In order to achieve the desired intimate mixing, it is preferred that smaller particle sizes be used. Suitable particle sizes for the titanium dioxide and the dopant are from about 1 microns to about 5 microns, with particle sizes below 2 microns being preferred. Larger particle sizes may be used, but will tend to increase the time and/or amount of heat needed to complete the reaction in high yield. The titanium dioxide starting material may comprise any phase (e.g., brookite, rutile or anatase). Examples of suitable dopants include  $Nb_2O_5$ ,  $NbO_2$ ,  $Ta_2O_5$ ,  $WO_3$ ,  $ZrO_2$ ,  $Fe_2O_3$ , etc.

The amount of dopant material that is mixed with the titanium dioxide is determined stoichiometrically based on the desired value of x in the formula  $Ti_{1-x}M_xO_{2-y}$ .

When wet mixing is used, it is desirable to add a dispersant to prevent agglomeration of the titanium dioxide and dopant particles. Suitable dispersants are well known and include inorganic acids, inorganic bases, organic acids, organic bases, poly(acrylic acid), salts of poly(acrylic acid), poly(methacrylic acid), salts of poly(methacrylic acid), copolymers of poly(acrylic acid), salts of copolymers of poly(acrylic acid), copolymers of poly(methacrylic acid), salts of copolymers of poly(methacrylic acid), poly(ethyleneimine), polyvinylpyrrolidone,

polyacrylamide, lignosulfonates, poly(ethylene oxide), adducts of ethylene oxide, adducts of propylene oxide, polycarboxylates, salts of polycarboxylates, naphthalene sulfonates, sulfosuccinates, polyphosphates, sodium silicates, phosphate esters, and mixtures thereof. An example of a suitable commercially available dispersant is sold under the name "Darvan® 821A" (R. T. Vanderbilt Corp.). A suitable amount of dispersant is, for example, about 0.5% of the total weight of the titanium dioxide and dopant materials.

After wet mechanical mixing, the mixture is dried, such as by spray drying, to recover a powder.

In order to improve material handling properties, such as flowability and pumpability, of the mixture of titanium dioxide and dopant, it may be desirable to add a small amount of a binder, such as polyvinylacetate. When a binder is used, it is typically used in an amount of about 1% or less by weight. When a binder is used, it will decompose at the reaction temperatures, and, therefore, will not appreciably affect the properties of the reaction product.

The reaction of the titanium dioxide with the dopant is typically conducted at a temperature of from about 1100°C to about 1400°C, with the reaction time being from about 30 minutes to several hours. For any particular mixture, there is a tradeoff between temperature and reaction time, i.e., the reaction will proceed to completion more quickly at higher temperatures. During the heating process, the element M (e.g., niobium) from the dopant is incorporated into the titanium dioxide structure (anatase, rutile or brookite), and any anatase or brookite is rearranged to form rutile. The incorporation of the dopant element (M) into the titanium dioxide structure, and any rearrangement from brookite or anatase to rutile, is preferably achieved before oxygen is removed from the crystal lattice to prevent formation of the Magneli phases. The desired incorporation of dopant element and any necessary rearrangement from anatase or brookite to rutile may be achieved in a reducing atmosphere by initially heating the mixture to a temperature at which substitution of the dopant element into the titanium dioxide structure and rearrangement occur at an appreciable rate, but oxygen removal from the crystal lattice does not occur at an appreciable rate, and gradually increasing the temperature of the mixture to a level at which oxygen removal does occur at an appreciable rate. Alternatively, the desired conductive, doped titanium oxide materials may be prepared by heating the mixture in an oxygen atmosphere to cause a dopant element in the mixture to become incorporated into the titanium dioxide

structure, and to cause any brookite or anatase to be converted to rutile, and subsequently removing the oxygen atmosphere and replacing it with a reducing atmosphere. An example of a suitable reducing atmosphere is an atmosphere comprised of a mixture of hydrogen and nitrogen. Higher hydrogen concentrations are more effective (i.e., result in faster removal of oxygen from the crystal lattice). However, for purposes of safety a hydrogen content of about 5% by weight may be preferred.

Suitable apparatuses for heating the mixture to achieve the desired reaction include rotary furnaces, push or belt furnaces, and batch furnaces. Rotary furnaces are preferred because of their ability to achieve complete reaction in a residence time of as little as about 30 minutes, whereas a typical reaction time for a push or belt furnace is about 5.5 hours using the same temperatures and reactants. Batch furnaces are not preferred because they require heating and cooling of the furnace for each batch.

After the reactions have been completed (i.e., incorporation of a dopant element into the titanium structure, any rearrangement from anatase or brookite to rutile, and a desired amount of oxygen removal from the crystal lattice), the product is preferably allowed to cool in an oxygen-free atmosphere to prevent oxygen from being incorporated into the crystal lattice. It is desirable that the product is allowed to cool in an oxygen-free atmosphere to a temperature of about 300°C or less, more preferably to a temperature of about 100°C or less, and even more preferably to a temperature of about 50°C or less.

In Fig. 8, there is shown a cutaway view of an alkaline battery, including a steel can 10 having a cylindrical shape. A cathode 32 formed of a mixture comprising manganese dioxide, a conductive, doped titanium oxide compound in accordance with the invention, graphite, potassium hydroxide solution, de-ionized water, an aqueous solution, and additives, is formed about the interior surface of can 10. A separator 36 is located about the interior surface of cathode 32. An electrolyte 30 formed of potassium hydroxide is disposed in the interior of separator 36. An anode, which may be formed of zinc powder, a gelling agent and other additives, is disposed within electrolyte 30 in contact with a current collector 34. The alkaline battery shown in Fig. 8 is illustrative of a battery employing the conductive, doped titanium oxide materials of this invention in an electrode of a battery. However, those having ordinary skill in the art will understand that the doped titanium dioxides of this invention may be

employed in various other types of batteries, including both primary and secondary batteries, and in batteries having various configurations.

Certain aspects of the invention are described below with respect to specific illustrative examples. These examples are intended to facilitate understanding of the principles and advantages of the invention. However, the scope of the invention is to be determined by the appended claims, and is not limited by the illustrative examples.

### Example 1

$\text{TiO}_2$  was reduced with  $\text{H}_2$  by heating  $\text{TiO}_2$  for 100 minutes at  $980^\circ\text{C}$  in a hydrogen atmosphere (5%  $\text{H}_2$  in  $\text{N}_2$  was used for safety, though a higher concentration would be more effective.) The reduced material was a fine powder that did not require grinding and sieving before use. Dry cathode mix was prepared by blending EMD and synthetic graphite, in a 25:1 ratio (by weight), in an analytical mill (Techmar model A-10) for 15 seconds, except that 1.6 wt% of the EMD, based on the total cathode weight, was replaced with niobium-doped  $\text{TiO}_2$  as a cathode additive. The EMD used was from Kerr McGee and the graphite was grade GA17 from Superior Graphite. The  $\text{TiO}_2$  used was anatase and the reduced n- $\text{TiO}_2$  was rutile.

### Example 2

Anatase  $\text{TiO}_2$  was doped with  $\text{Nb}_2\text{O}_5$  by: (a) mixing the desired weight ratios of  $\text{TiO}_2$  and  $\text{Nb}_2\text{O}_5$  with a mortar and pestle, along with methanol for easier homogenization, (b) pressing the mixture into a pellet, (c) sintering at  $1200^\circ\text{C}$ - $1250^\circ\text{C}$  for 20 hours, and (d) milling. Steps (c) and (d) were repeated for a total of 80 hours of sintering.  $\text{TiO}_2$  was doped with both 10 wt% and 20 wt%  $\text{Nb}_2\text{O}_5$ . The sintering temperature was  $1200^\circ\text{C}$  for the material with 10% dopant and  $1250^\circ\text{C}$  for the material with 20% dopant. The  $\text{Nb}_2\text{O}_5$ -doped  $\text{TiO}_2$  had a rutile structure. It was then prepared for use by grinding with a mortar and pestle and sieving through a  $53\ \mu\text{m}$  sieve. Dry cathode mix was prepared in the same manner as in Example 1, but using  $\text{Nb}_2\text{O}_5$ -doped  $\text{TiO}_2$  as the additive.

The resistances of the dry cathode mixes described were tested by placing three grams of dry mix into a cylinder made of an electrically nonconductive material, having a 0.50 inch inside diameter and having an electrically conductive base pad. The mix was compressed with an

electrically conductive plunger, and the resistance was measured between the plunger and pad during compression of the mix. Results of the resistance test are shown in Fig. 1, which shows the cathode resistance in ohms as a function of pressure in pounds per square inch. Each curve represents the average of three samples. The curve labeled "+1.6% TiO<sub>2</sub>" represents the cathode mix with anatase TiO<sub>2</sub> as an additive, the curve labeled "TiO<sub>2</sub>+H<sub>2</sub>" represents the cathode mix with hydrogen-reduced TiO<sub>2</sub> as an additive, the curve labeled "TiO<sub>2</sub>+10%Nb<sub>2</sub>O<sub>5</sub>" represents the cathode mix with TiO<sub>2</sub> doped with 10 wt% Nb<sub>2</sub>O<sub>5</sub>, and the curve labeled "TiO<sub>2</sub>+20%Nb<sub>2</sub>O<sub>5</sub>" represents the cathode mix with TiO<sub>2</sub> doped with 20wt% Nb<sub>2</sub>O<sub>5</sub>. These curves show that the mix containing hydrogen-reduced TiO<sub>2</sub> and the mix containing Nb<sub>2</sub>O<sub>5</sub>-doped TiO<sub>2</sub> have lower resistance than the mix containing anatase TiO<sub>2</sub>.

Miniature alkaline Zn/MnO<sub>2</sub> cells were made and discharged to evaluate the effects on cell capacity when using doped or hydrogen-reduced TiO<sub>2</sub> as a cathode additive. A portion of each of the cathode mixes from Examples 1 and 2 was mixed with 3 wt% of 45% aqueous KOH solution and blended with a mortar and pestle for 5 minutes to produce a wet mix. The wet mix was formed into pellets weighting 0.7175 gram. Each pellet was placed into an IEC R44-size nickel-plated steel can with an inside diameter of 0.447 inch. The can served as the cathode container and positive terminal of the cell. A nickel mesh screen 0.447 inch in diameter was placed on top of the pellet as the current collector, and the pellet was compressed with a hydraulic press to a height of approximately 0.085 inch from the inside surface of the can bottom, producing a formed cathode with about 72 percent solids packing by volume. Two separator discs were placed in the can on top of the formed cathode. A fixture to hold the anode was placed on the top of the can, and an excess amount of gelled anode, based on the theoretical capacity of the cathode pellet, was put into the fixture. The anode contained 70 wt% zinc powder in a 37 wt% aqueous KOH solution gelled with Carbopol. An indium-burnished brass nail was inserted into the anode gel from the top of the anode fixture as a current collector. Each cell was discharged continuously at 85.5 mA to 1.0 volt. This discharge rate was selected because the current density is about equivalent to a 1000 mA discharge rate in an IEC LR6 size cell, based on the interfacial surface area. Results of this test are shown in Fig. 2. Cells with both the

hydrogen-reduced and 10% Nb<sub>2</sub>O<sub>5</sub>-doped TiO<sub>2</sub> cathode additives performed significantly better than cells with an untreated anatase TiO<sub>2</sub> additive. Cells with 20% Nb<sub>2</sub>O<sub>5</sub> as the cathode additive performed poorly even though the cathode resistance (Fig. 1) was low. It is believed that the capacity was low because not all of the Nb<sub>2</sub>O<sub>5</sub> was doped into the TiO<sub>2</sub>, so there was an excess of Nb<sub>2</sub>O<sub>5</sub> present. The cells with hydrogen-reduced TiO<sub>2</sub> additive did not perform as well as would be expected based solely on the cathode resistance test results, possibly due to poor stability of hydrogen-reduced TiO<sub>2</sub> with EMD in the KOH electrolyte.

### Example 3

Dry cathode mixes were made as described in Example 1, except with EMD:graphite weight ratios of 15:1 and 20:1, rather than 25:1. At each of these two EMD:graphite levels, one mix was made with no cathode additive and the other was made with 1.6 wt% of 10% Nb<sub>2</sub>O<sub>5</sub>-doped TiO<sub>2</sub> added, as described in Example 2. Each dry mix was made into a wet mix, pellets were formed and put into cans, and formed cathodes were made as described in Example 2, except that no separators were put into the cans. Each of the formed cathodes was discharged in flooded half cells at 85.5 mA to 1.18 volt, against a zinc reference electrode. The reference electrode contained zinc metal in a gelled 37% aqueous KOH solution. The results of the flooded half cell testing are summarized in Figs. 3-5. Fig. 3 shows the relative discharge durations. At both EMD:graphite ratios, the cells with the doped TiO<sub>2</sub> additive performed better than the cells with no additive. The actual discharge curves are shown in Figs. 4 and 5.

### Example 4

A series of AAA size batteries were prepared with a cathode composition comprising 93.22 wt% electrolytic manganese dioxide (EMD), 3.68 wt% graphite, 3.05 wt% of a 45% aqueous potassium hydroxide solution, and 0.05 wt% of polytetrafluoroethylene (PTFE) binder. The anode composition comprised 70.00 wt% zinc, 0.02% In(OH)<sub>3</sub>, 0.42% gelling agent, 1.17 wt% de-ionized water, and the balance being a potassium hydroxide solution at a concentration sufficient to provide a potassium hydroxide concentration of 37% in the cell electrolyte after assembly. Each cell contained 4.96 grams of the cathode composition and an excess of the anode composition, with an additional 0.95 grams of 37% potassium hydroxide solution added to each cell. The cells were prepared in a conventional manner. The basic steps in cell construction



include making a cathode mixture, forming the cathode mixture into rings, inserting the rings into a cell container (can) and compressing the ring to form a cathode with a central cavity, inserting a separator into the central cavity of the cathode, making an anode mixture, depositing the anode mixture in the cavity of the cathode with the separator disposed between the cathode and the anode, adding additional electrolyte solution, and adding an appropriate anode collector and seal for the cell. These cells were used as a standard or control for evaluating batteries prepared with the additives of this invention.

A second series of AAA cells was prepared in a substantially identical manner except that a portion of the EMD was replaced with a conventional anatase titanium dioxide additive so that the cathode contained 1.6% of the additive by weight, or a weight ratio of additive to EMD of about 0.018 to 1.

A third series of AAA cells was prepared that was identical to the second set, except that the conventional anatase titanium dioxide additive was replaced with a niobium-doped rutile titanium oxide in accordance with the invention.

On average, when cells were subjected to a 400 mA continuous discharge to 0.9 volts, the cells containing the anatase did not exhibit an improvement over the control cells. The cells containing a niobium-doped titanium oxide in accordance with the invention exhibited a 4% service improvement over the control cells. At a higher current drain the cells containing a niobium-doped rutile titanium dioxide additive in accordance with the invention outperformed the cells containing the conventional anatase titanium dioxide additive. In particular, the test cells in accordance with the invention exhibited a 3% service improvement over the control cells, whereas the cells containing the anatase additive did not perform as well as the control cells, when subjected to a 600 mA continuous discharge to 0.9 volts. In separate testing, even cells with half the amount of niobium-doped rutile titanium dioxide performed better than cells with no additive or cells with a 0.018 to 1 anatase  $\text{TiO}_2$  to EMD weight ratio. Even lower levels of the NTO additive of the present invention may be sufficient for improving performance.

### Example 5

Another series of tests substantially identical to those in Example 4 were conducted, except the final potassium hydroxide concentration in the electrolytes in the AAA cells was 35% rather than 37%. In these tests, cells containing an additive in accordance with the invention

significantly outperformed cells containing a conventional anatase titanium dioxide additive. For the 400 mA continuous discharge to 0.9 volts, the cells containing a niobium-doped rutile titanium dioxide additive of the invention exhibited a 15% service improvement with respect to the control, whereas the cells containing the anatase titanium dioxide additive only exhibited a 4% improvement with respect to the control. At a 600 mA continuous discharge to 0.9 volts, the cells containing a niobium-doped rutile titanium dioxide additive in accordance with the invention exhibited a 25% service improvement as compared with the control, whereas the cells containing the anatase additive did not perform as well as the control cells.

#### Example 6

A series of tests similar to those in Examples 4 and 5 were conducted on additives in accordance with the invention to determine the effect of particle size of the additive on service improvement. Additives having an average particle size of 15 microns, 60 microns and 84 microns were tested. All of the additives provided service improvement on both the 400 mA and 600 mA continuous discharge tests. However, the smaller particle sizes appeared to provide the greatest service improvement.

Although the electrochemical cell of the present invention has been described in the above examples as a primary  $\text{Zn/MnO}_2$  cell having an aqueous KOH electrolyte, it will be appreciated by those skilled in the art that the present invention may be used for primary and rechargeable cells and cells of other electrochemical systems, anode-cathode pairs and/or electrolytes.

It will be understood by those who practice the invention and those skilled in the art that various modifications and improvements may be made to the invention without departing from the spirit of the disclosed concept.

What is claimed:

1. An alkaline electrochemical battery cell comprising an anode, a cathode, a separator between the anode and cathode, and an electrolyte, wherein at least one of the anode, cathode and electrolyte contains an n-type metal oxide additive.
- 5 2. The cell according to claim 1, wherein the electrolyte is an aqueous electrolyte.
3. The cell according to claim 1, wherein the n-type metal oxide additive is a doped metal oxide, comprising a metal oxide modified by incorporation of a dopant.
- 10 4. The cell according to claim 1, wherein the n-type metal oxide additive is a reduced metal oxide.
5. The cell according to claim 3, wherein the metal oxide is selected from the group consisting of  $\text{BaTiO}_3$ ,  $\text{K}_2\text{TiO}_3$ ,  $\text{CoTiO}_3$ ,  $\text{SrTiO}_3$ ,  $\text{CaTiO}_3$ ,  $\text{MgTiO}_3$ ,  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{TiO}_2$ ,  $\text{CoO}$ ,  
 15  $\text{Co}_3\text{O}_4$ ,  $\text{ZnO}$ ,  $\text{SnO}$ ,  $\text{SnO}_2$ ,  $\text{PbO}_2$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3 \cdot 3\text{ZrO}_3$ ,  $\text{Bi}_{12}\text{TiO}_{20}$ ,  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{CaWO}_4$ ,  $\text{ZnMn}_2\text{O}_4$ , and  $\text{K}_2\text{Cr}_2\text{O}_7$ .
6. The cell according to claim 3, wherein the metal oxide is selected from the group consisting of  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{SnO}_2$ .
- 20 7. The cell according to claim 3, wherein the dopant comprises a cation that, when added to the structure of the undoped metal oxide, reduced the resistivity of the metal oxide.
8. The cell according to claim 7, wherein the metal oxide is  $\text{TiO}_2$  and the dopant is selected  
 25 from the group consisting of  $\text{NbO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{WO}_3$ ,  $\text{GeO}_2$ ,  $\text{ZrO}_2$ ,  $\text{SnO}_2$ ,  $\text{ThO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{LiNiO}_2$  and  $\text{P}_2\text{O}_5$ .

9. The cell according to claim 8, wherein the dopant is  $\text{Nb}_2\text{O}_5$ .
10. The cell according to claim 6, wherein the metal oxide is  $\text{SnO}_2$  and the dopant is selected from the group consisting of  $\text{In}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{WO}_3$  and  $\text{P}_2\text{O}_5$ .

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11. The cell according to claim 1, wherein the metal oxide additive is initially contained in the cathode.

12. The cell according to claim 2, wherein the anode comprises zinc and the cathode  
10 comprises  $\text{MnO}_2$ .

13. The cell according to claim 12, wherein the metal oxide is  $\text{TiO}_2$  and the dopant is  $\text{Nb}_2\text{O}_5$ .

15 14. The cell according to claim 13, wherein the n-type metal oxide has an average particle size of about 60 microns or less.

15. The cell according to claim 14, wherein the average particle size is 15 microns or less.

20 16. The cell according to claim 15, wherein the average particle size is 1 to 5 microns.

17. The cell according to claim 16, wherein the average particle size is 1 to 2 microns.

18. The cell according to claim 1, wherein the n-type metal oxide has a resistivity less than  
25 100 ohm-cm.

19. The cell according to claim 18, wherein the resistivity is 10 ohm-cm or less.

9. The cell according to claim 8, wherein the dopant is  $\text{Nb}_2\text{O}_5$ .

10. The cell according to claim 6, wherein the metal oxide is  $\text{SnO}_2$  and the dopant is selected from the group consisting of  $\text{In}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{WO}_3$  and  $\text{P}_2\text{O}_5$ .

5

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15 14. The cell according to claim 13, wherein the n-type metal oxide has an average particle size of about 60 microns or less.

15. The cell according to claim 14, wherein the average particle size is 15 microns or less.

20 16. The cell according to claim 15, wherein the average particle size is 1 to 5 microns.

17. The cell according to claim 16, wherein the average particle size is 1 to 2 microns.

25 18. The cell according to claim 1, wherein the n-type metal oxide has a resistivity less than 100 ohm-cm.

19. The cell according to claim 18, wherein the resistivity is 10 ohm-cm or less.

20. An alkaline electrochemical battery cell comprising a zinc-containing anode, a manganese dioxide-containing cathode, a separator between the anode and cathode, and an aqueous alkaline electrolyte, wherein at least one of the anode, cathode and electrolyte contains a niobium-doped  $\text{TiO}_2$  additive having a resistivity less than 100 ohm-cm.

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21. The cell according to claim 20, wherein the electrolyte comprises 35 to 37 weight percent potassium hydroxide.

10 22. The cell according to claim 20, wherein the weight ratio of niobium-doped  $\text{TiO}_2$  to  $\text{MnO}_2$  is 0.018 to 1 or less.

23. The cell according to claim 22, wherein the weight ratio of niobium-doped  $\text{TiO}_2$  to  $\text{MnO}_2$  is 0.009 to 1 or less.

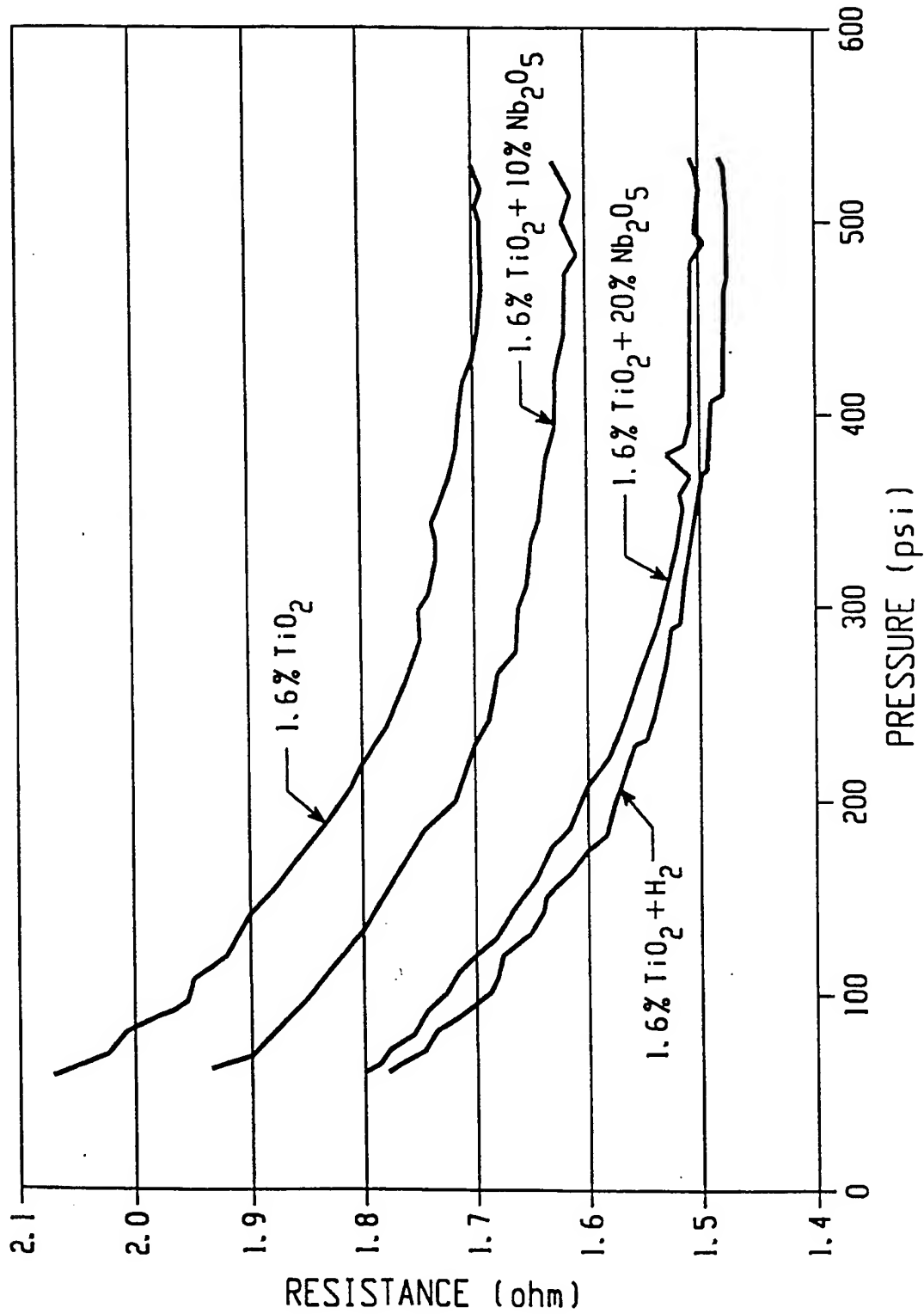


Fig. 1

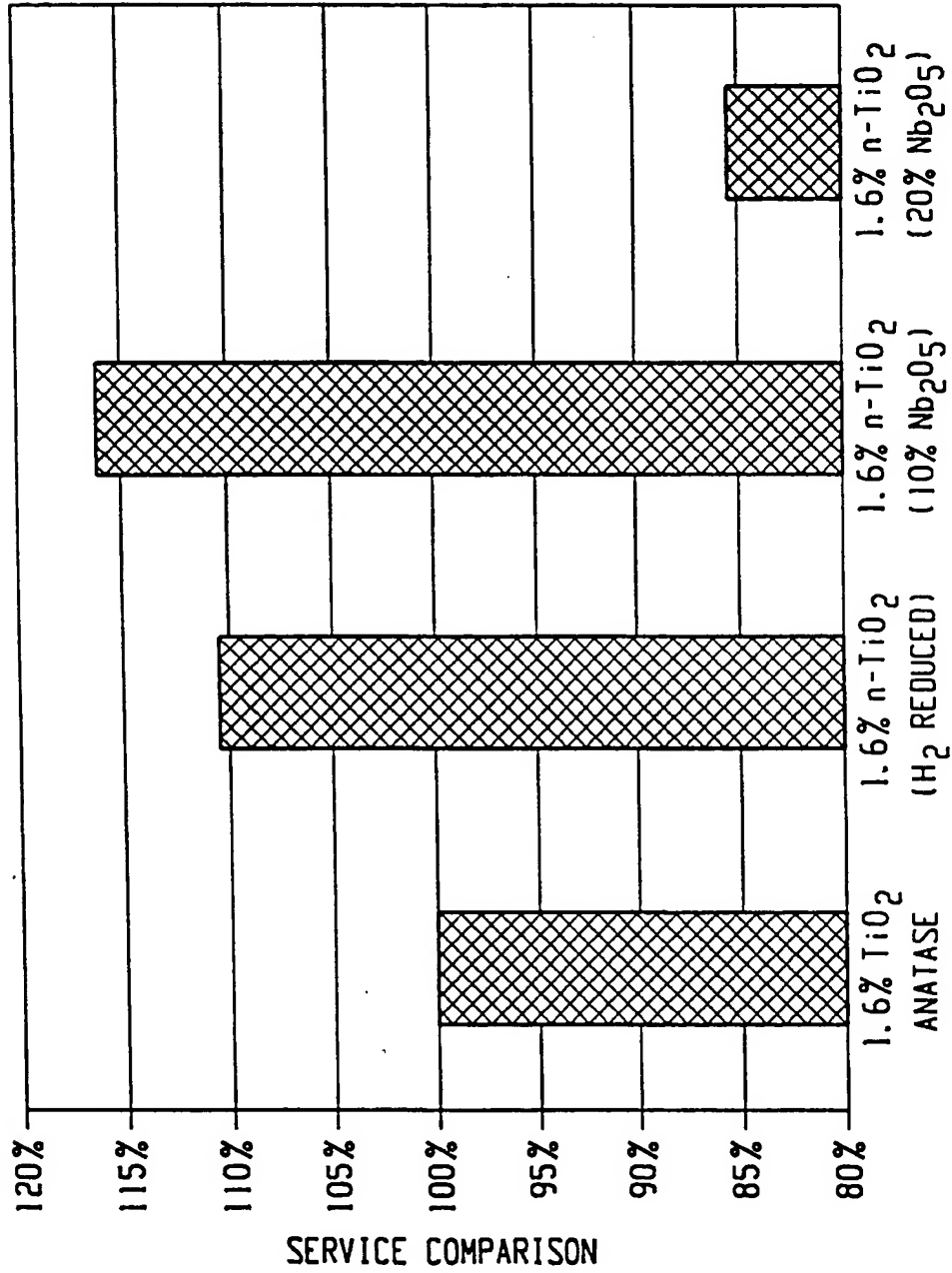


Fig. 2



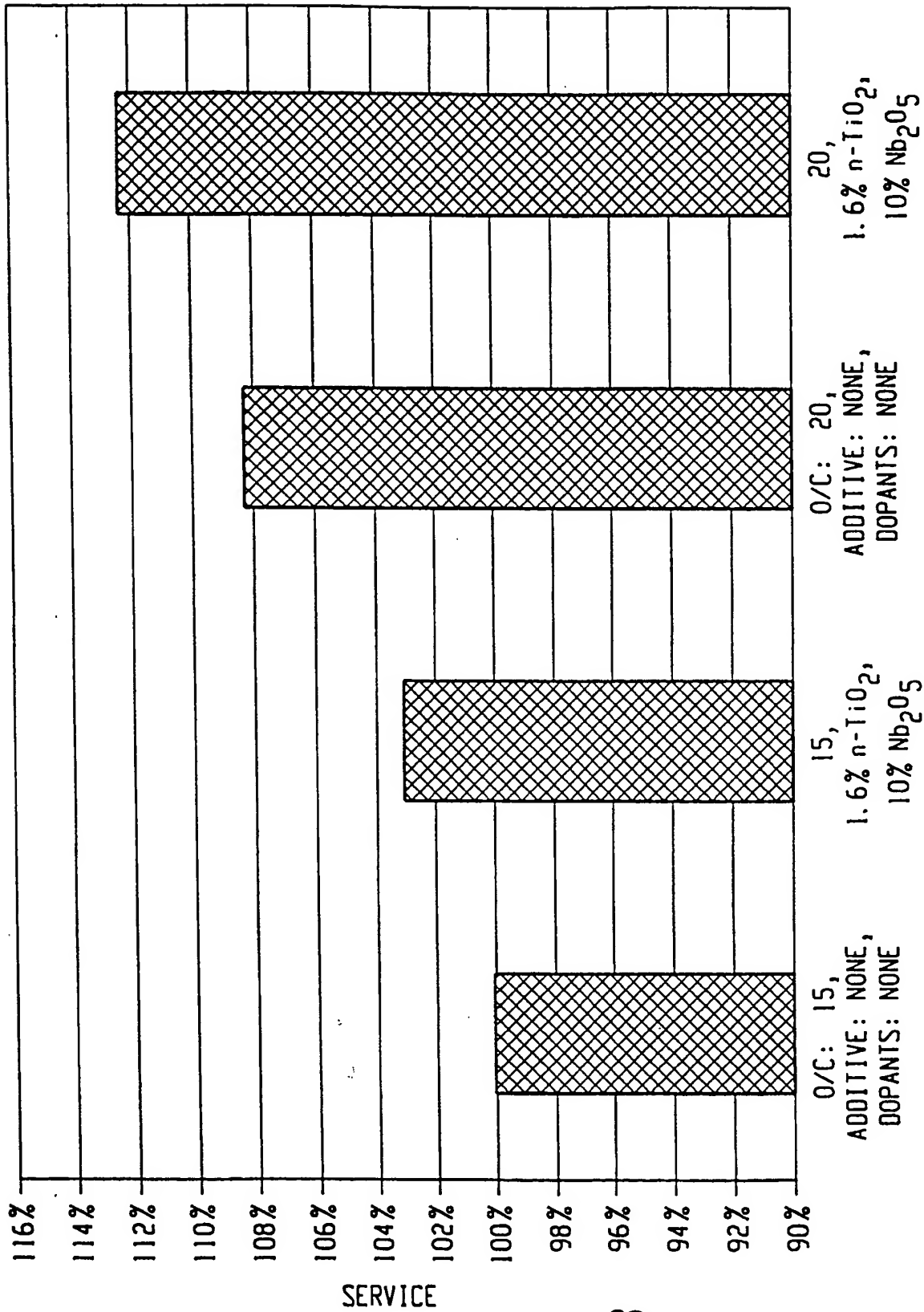


Fig. 3

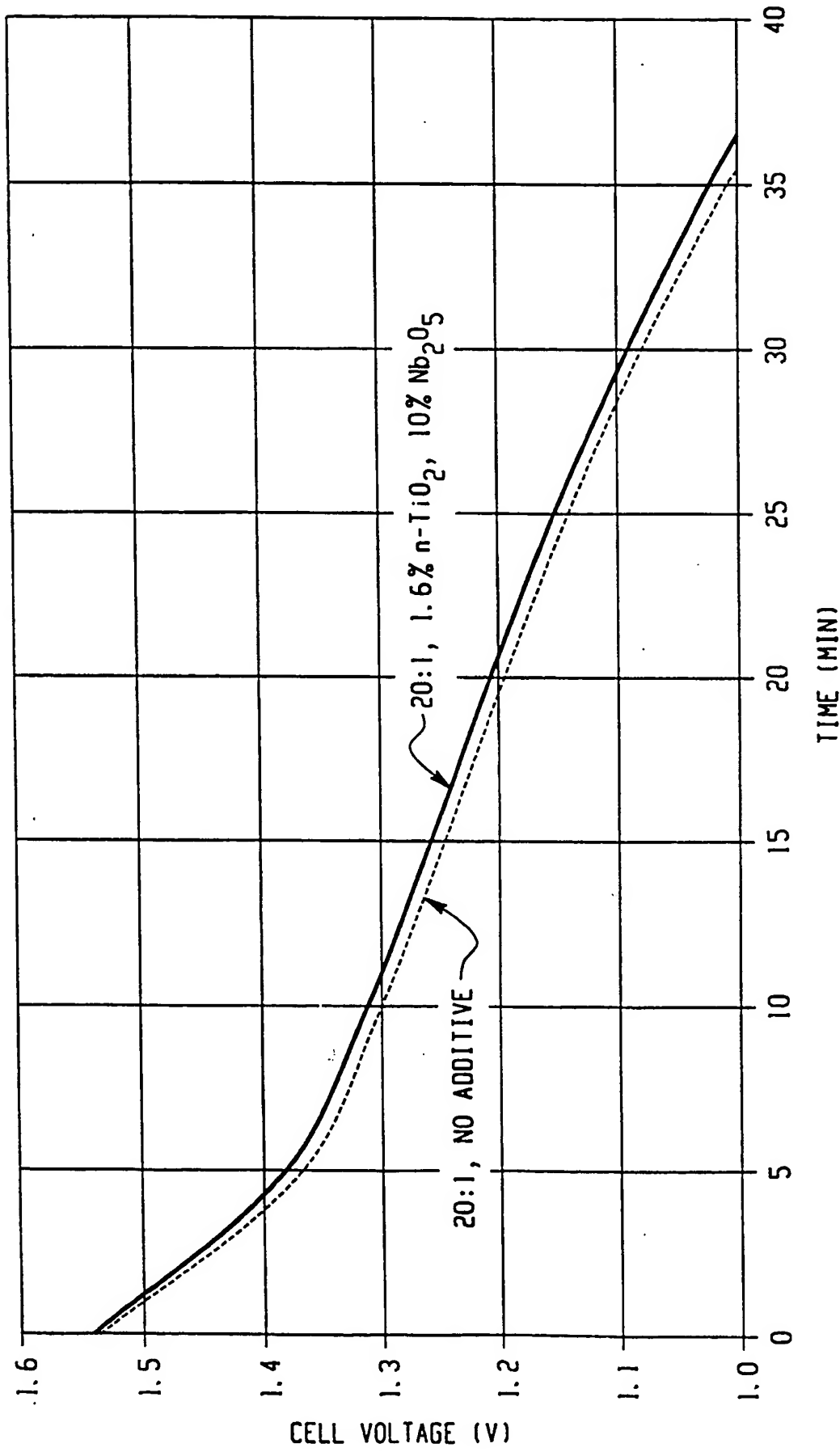


Fig. 5

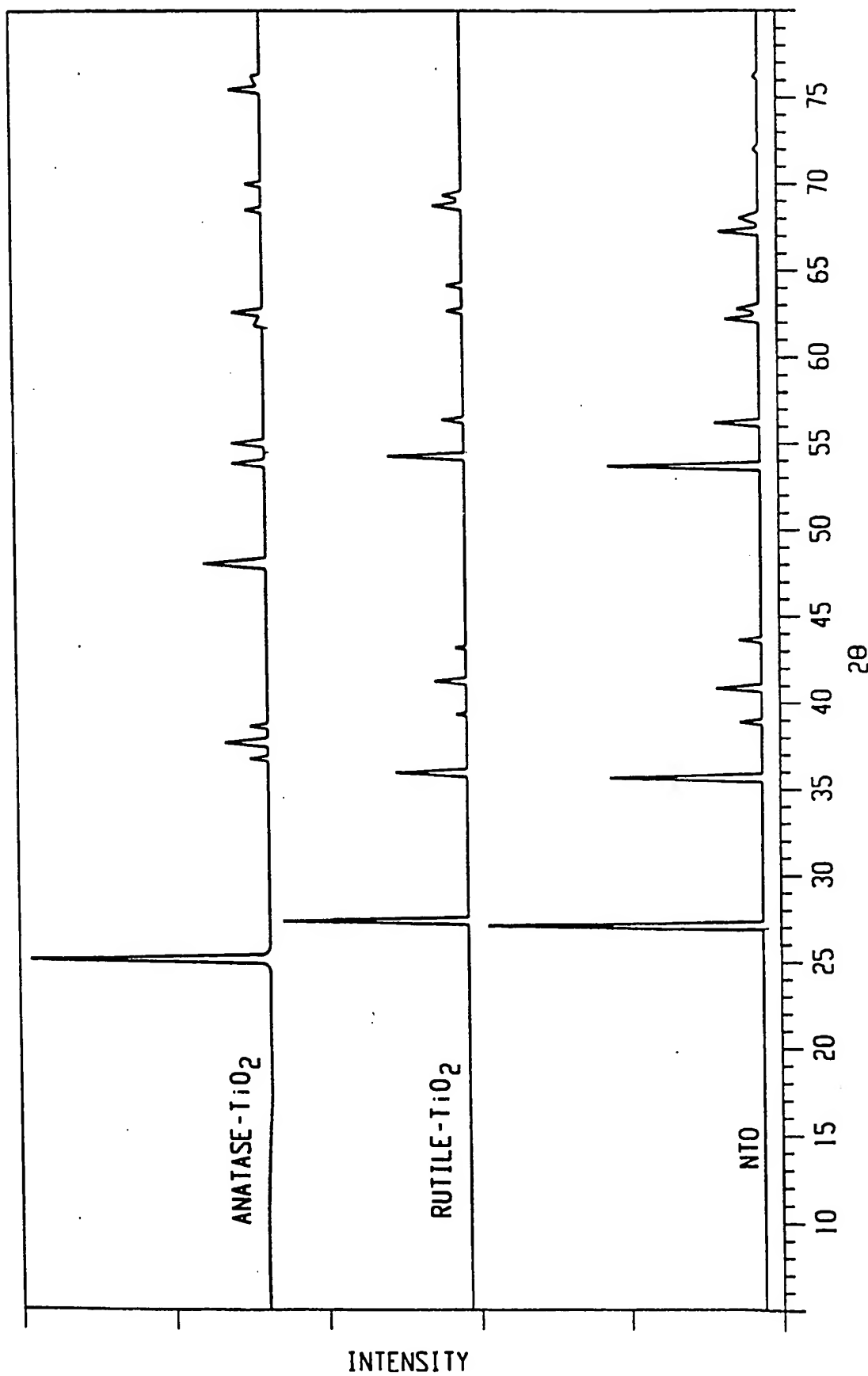


Fig. 6

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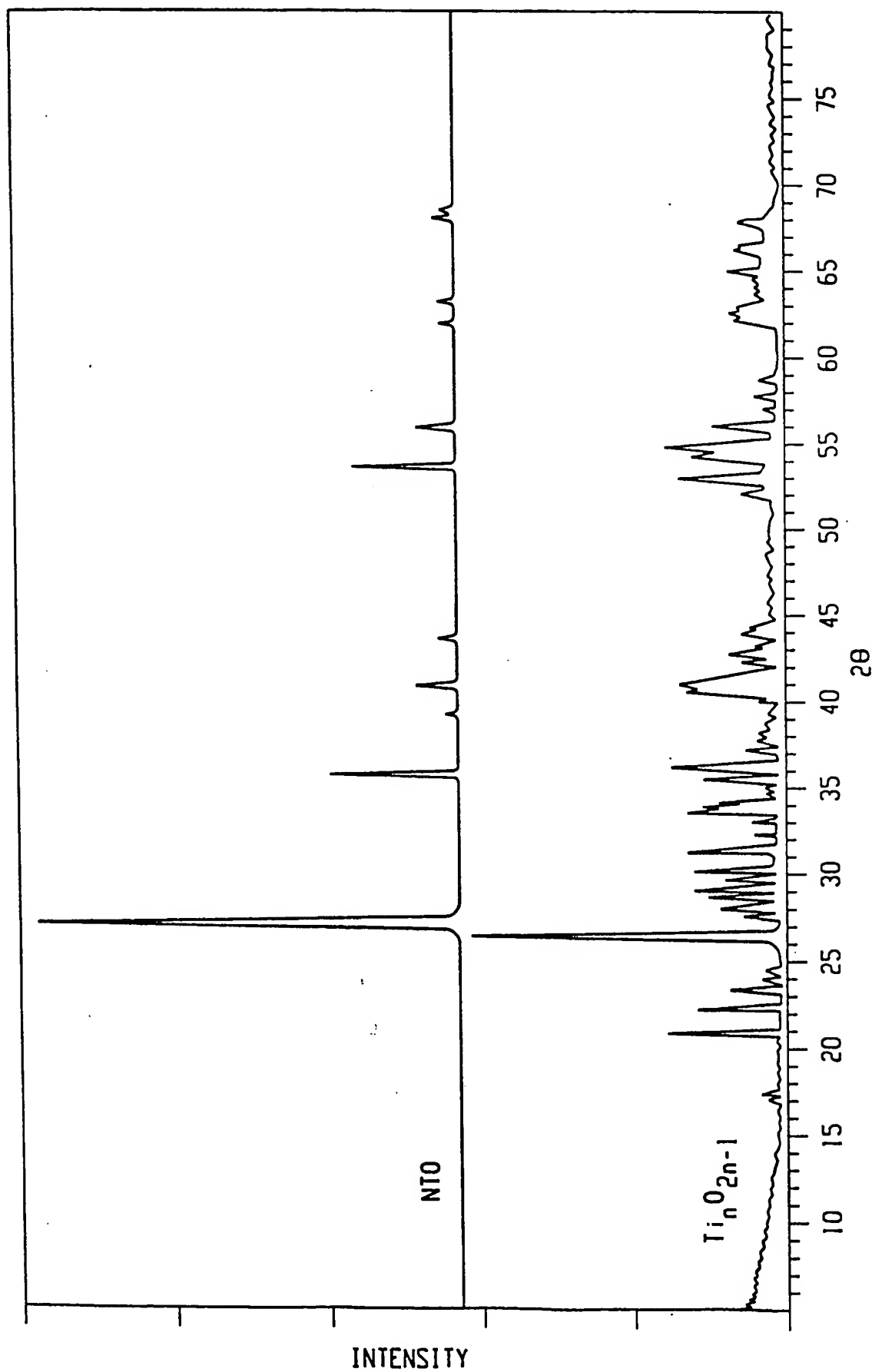
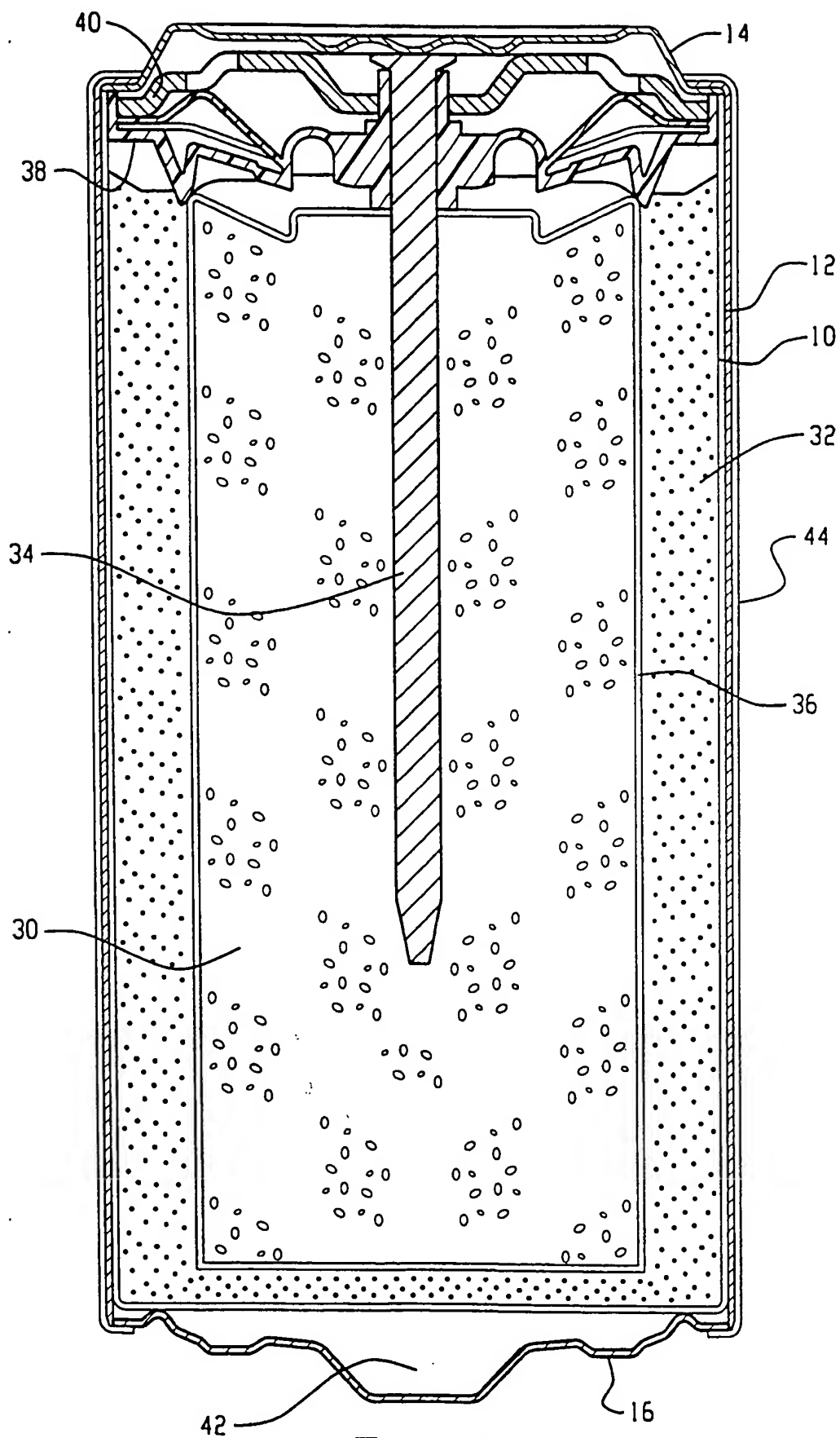


Fig. 7

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*Fig. 8*

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According to International Patent Classification (IPC) or to both national classification and IPC

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 747 982 A (EVEREADY BATTERY INC) 11 December 1996 (1996-12-11) claims 1-19 ---	1-3, 5-8, 13
X	WO 98 15987 A (MERCK PATENT GMBH ;PFAFF GERHARD (DE); GLAUSCH RALF (DE); HILARIUS) 16 April 1998 (1998-04-16) page 7, line 10 - line 15; claims 1-10 ---	1-3, 5-7
A	US 5 532 085 A (DAVIS STUART M ET AL) 2 July 1996 (1996-07-02) claims 1-14 ---	1-23
A	WO 92 17910 A (BATTERY TECHNOLOGIES INC) 15 October 1992 (1992-10-15) claims 1-4 ---	1-23
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

\*P\* document published prior to the international filing date but later than the priority date claimed

**'&' document member of the same patent family**

Date of the actual completion of the international search

29 September 2000

Date of mailing of the international search report

18/10/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Battistiq, M

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/17561

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 195 46 333 A (GRILLO WERKE AG) 20 June 1996 (1996-06-20) claims 1-7	1-23
A	US 5 895 734 A (NARDI JOHN C ET AL) 20 April 1999 (1999-04-20) claims 1-4	1-23

# INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/US 00/17561

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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